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## USE OF UNCONVENTIONAL METHODS OF OBTAINING CORDIERITE CERAMIC PIGMENTS

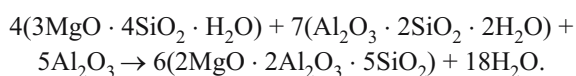
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The possibility of obtaining cordierite ceramic pigments from mixtures of talc, kaolin, and alumina by boiling and autoclaving is investigated. It is found that autoclave treatment and boiling for the preparation of a charge to be used in obtaining ceramic pigments is desirable and promising, because this method makes it possible to neutralize, to the extent possible, and homogenize the components of the charge. Autoclaving is a more difficult method than boiling and requires a special airtight apparatus — an autoclave, but it yields pigments with more stable and saturated color.

Natural talc is a conventional raw material for obtaining cordierite, steatite, and forsterite ceramics. Talc with the appropriate admixture of pure oxides can be used to synthesize ceramic pigments with the structures of magnesium metasilicate, forsterite, and diopside [1, 2].

Ceramic pigments with cordierite structure are obtained by solid-phase synthesis from mixtures of pure oxides at optimal temperature 1320°C [3]. To synthesize cordierite, different initial substances where the oxide content is determined by the stoichiometric composition of the cordierite, can be used to prepare the charge mixtures. Usually, mixtures of talc, high-quality refractory clays, and technical alumina are used to obtain cordierite under commercial conditions. When such a mixture is heated, first these compounds undergo degradation, after which the following reaction occurs:



However, in practice, the reaction does not proceed in complete agreement with this equation. Besides cordierite, clinoenstatite  $\text{MgO} \cdot \text{SiO}_2$  and mullite  $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$  are formed [4].

When these mixtures are calcined, cordierite first forms in the temperature range 1000–1270°C. Cordierite formation occurs actively at temperatures 1200–1400°C. When temperature increases to 1450°C, cordierite melts and decomposes. The rate of the solid-phase reaction is regulated by introducing additives [5]. Some investigators used as mineralizers low-melting and volatile fluorides, chlorides, and oxides in amounts 5–10%. The introduction of these compounds decreased the synthesis temperature to 800–1000°C.

Most natural minerals are prone to isomorphic substitutions in the crystal structure. But the possibilities of these substitutions are limited. To intensify the penetration of chromophoric ions into the crystal lattice of natural minerals, mineralizers or unconventional methods for obtaining ceramic pigments must be used [6].

Different technical methods exist for careful mixing of the components of a charge and for process activation during the production of ceramic pigments: simultaneous grinding in planetary mills, coprecipitation of salts from water solutions, and saturation of finely milled mineral components with a water solution of salts of the coloring metals. There is also a method for obtaining inorganic pigments by boiling

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TABLE 1.

Raw material	Mass content, %							
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	TiO <sub>2</sub>	R <sub>2</sub> O	calcination losses
Onotskoe talc	61.27	0.61	0.41	0.50	32.23	—	—	4.98
Prosyankovskoe kaolin	46.73	37.43	0.72	0.71	0.65	0.47	0.18	13.12

TABLE 2.

Pigment by means of		Salt	Mass content in solution, %	Chromophore ion	Mass content, %
boiling	autoclaving				
K1	A1	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	24.8	$\text{Fe}^{2+}$	5
K2	A2	$\text{CuSO}_4$	12.6	$\text{Cu}^{2+}$	5
K3	A3	$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$	18.0	$\text{Mn}^{2+}$	5
K4	A4	$\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$	25.6	$\text{Cr}^{3+}$	5
K5	A5	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	24.7	$\text{Ni}^{2+}$	5
K6	A6	$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	24.8	$\text{Co}^{2+}$	5
K7	A7	$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} + \text{CrCl}_3 \cdot 6\text{H}_2\text{O}$	4.9 + 20.5	$\text{Co}^{2+} : \text{Cr}^{3+}$	1 : 4
K8	A8	$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} + \text{CrCl}_3 \cdot 6\text{H}_2\text{O}$	19.7 + 5.1	$\text{Co}^{2+} : \text{Cr}^{3+}$	4 : 1
K9	A9	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O} + \text{MnCl}_2 \cdot 4\text{H}_2\text{O}$	9.93 + 7.2	$\text{Fe}^{2+} : \text{Mn}^{2+}$	2 : 2
K10	A10	$\text{CrCl}_3 \cdot 6\text{H}_2\text{O} + \text{CuSO}_4$	20.5 + 2.5	$\text{Cr}^{3+} : \text{Cu}^{2+}$	4 : 1

natural minerals in a solution of salts (USSR Inventor's Certificate No. 1353787).

Our goal in the present work was to obtain cordierite ceramic pigments from a mixture of talc, kaolin, and alumina by means of boiling and autoclaving.

Cordierite was synthesized according to the reaction indicated above. Enriched talc from the Onotskoe deposit and kaolin from the Prosyankovskoe deposit with main mineral contents 98 and 95%, respectively, were used as the main raw material.<sup>2</sup> Aluminum oxide was introduced in the form of G00 technical alumina. The chemical composition of the natural raw material is presented in Table 1.

The natural minerals were ground to No. 0063 sieve residue of not more than 2%. Talc and kaolin in amounts of 39.5% and 47.1%, respectively, were mixed together and 13.4% aluminum oxide was added (according to the reaction presented above) to obtain a stoichiometric composition of cordierite. This charge was placed in a solution of the coloring salt in the volume ratio 1 : 3 (mineral powder : chromophore solution). The chromophore solutions were prepared assuming maximum solubility of the salts, so as to obtain chromophoric ion content 4.0 – 5.0% of the solution depend-

ing on the type of salt. The initial composition of the salt solutions is presented in Table 2.

Compositions were prepared with one chromophore as well as with different combinations of coloring ions. The mixture was boiled for 1 h, after which the precipitate was filtered, dried at 120°C, and calcinated. The calcination temperature was varied in the range 1000 – 1200°C.

In addition, the possibility of obtaining cordierite ceramic pigments using stages of autoclaving to obtain more intense flow of diffusion processes when the chromophore ions were embedded in the crystal structure of the materials was investigated. The charge was prepared by the method described. A solution of the salts and the charge in a prescribed ratio were loaded into the autoclave. The prepared mixture was heated in the autoclave to temperature 170°C, which gives water vapor pressure 0.8 MPa. The mixture was held at this temperature and pressure for 1 h. Then the liquid was separated, and the precipitate was tried and calcined at 1000 – 1200°C. The sintered material was broken up to No. 0063 sieve residue of no more than 0.2%.

Pigments with diverse color were obtained as a result. Visual analysis showed that autoclaving and boiling in many cases give different color tones to pigments with the same composition; this is confirmed by the different values of the dominant wavelength in the reflection spectrum (Table 3). In

<sup>2</sup> Here and below — the mass content.

TABLE 3.

Chromophore ion	Boiling		Autoclaving		Pigment color*	
	Pigment color*	Wavelength, nm	Pigment color*	Wavelength, nm	Pigment color*	Wavelength, nm
$\text{Fe}^{3+}$	Red-brown	730	Orange brown	710	Red-brown	
$\text{Cu}^{2+}$	Yellow-brown	610	Sand	594	Turquoise	Gray-green
$\text{Ni}^{2+}$	Light green	570	Light green	573	Olive	
$\text{Co}^{2+}$	Light blue	478	Bright sky-blue	475	Blue	Bright blue
$\text{Cr}^{3+} - \text{Co}^{2+}$	Dark green	490	Grass green	550	Emerald	Blue-green
$\text{Cr}^{3+} - \text{Cu}^{2+}$	Light brown	600	Brownish green	603	Brown	Dark green

\* Firing temperature 1200°C.

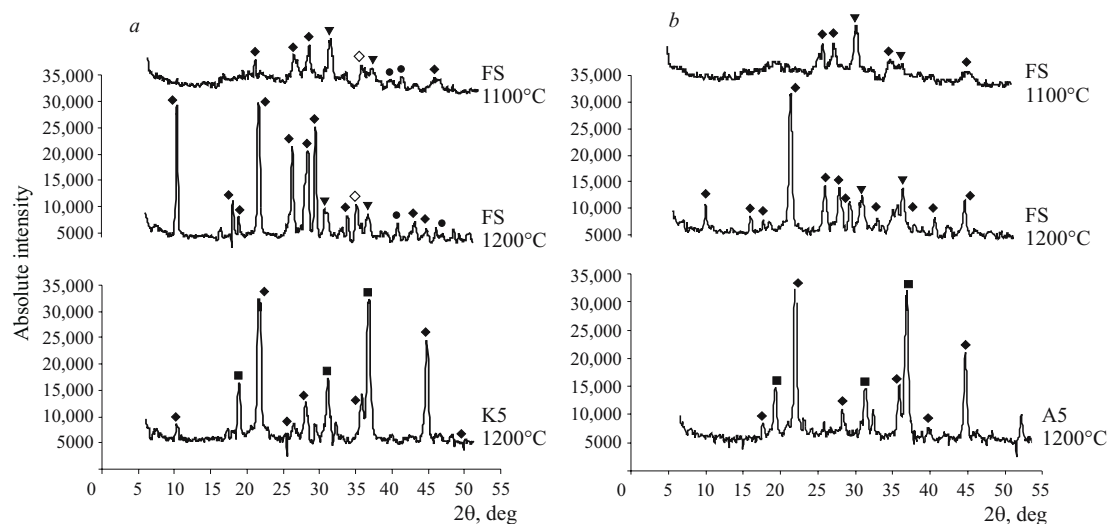


Fig. 1. Diffraction patterns of free samples (FS) and pigments obtained by the stages of boiling (a) and autoclaving (b):  $\blacklozenge$  cordierite;  $\blacktriangledown$  clinoenstatite  $\text{MgSiO}_3$ ;  $\bullet$  mullite;  $\diamond$  corundum;  $\blacksquare$  spinel.

addition, the coloration of the sinter cake of pre-autoclaved pigments is more uniform. This is explained by the fact that autoclaving gives more intense diffusion of the chromophore ions into the particles of the mineral charge and gives pigments with brighter and more stable color.

The pigments were tested for subglaze decoration of ceramic articles, which were fired at 1050°C. Under these conditions the pigments were found to be resistant to the effects of the glaze. Pigments with cobalt, iron, chromium, and nickel oxides are stable. Copper oxide imparts yellow-brown and sand color to pigments but when they interact with a glaze these pigments give turquoise and gray-green color. The colors of pigments containing nickel oxide change somewhat in subglaze decoration.

X-ray phase analysis showed that the cordierite structure forms in the temperature range 1100–1200°C (see Fig. 1). Peaks characteristic for the following crystal phases are identified in the diffraction patterns of free samples: cordierite — dominant phase ( $d = 0.854, 0.409, 0.202$  nm), clinoenstatite ( $d = 0.287, 0.252, 0.245$  nm), mullite ( $d = 0.269, 0.229$  nm). The free samples differ with respect to the intensity of some characteristic cordierite diffraction peaks. A higher intensity of cordierite peaks is observed for free samples obtained by boiling. Fewer diffraction peaks characteristic for intermediate reaction products are present for free samples obtained by autoclaving.

Well-expressed cordierite structure forms in pigments with cobalt oxide. In samples obtained by autoclaving, the intensity of the cordierite peaks is higher than in a free sample.

An almost identical diffraction pattern is seen for pigments with NiO which were obtained by autoclaving and boiling. At the same time the pattern differs strongly from the patterns of other samples. This is explained by the fact that a spinel phase ( $d = 0.466, 0.285, 0.243$  nm) forms together with cordierite. Judging from the intensity of the re-

flections, such an appreciable amount of spinel cannot be attributed solely to the formation of  $\text{NiAl}_2\text{O}_4$ . It is obvious that nickel ions, manifesting different degrees of oxidation, alter the reaction scheme, drawing magnesium ions present in the products of decomposition talc into formation of spinel.

The introduction of boiling and especially autoclaving stages makes it possible to accelerate diffusion processes and partially transfer them to low temperatures with the participation of a liquid phase (solution).

In summary, the use of autoclaving and boiling for preparation of the charge for obtaining ceramic pigments is desirable and promising, since this makes it possible to neutralize, to the extent possible, and homogenize the components of the charge. Autoclaving, as compared with boiling, is more laborious and requires a special airtight apparatus — an autoclave, but it yields pigments with more stable and saturated color.

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